



(11) **EP 4 202 008 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
28.06.2023 Bulletin 2023/26

(21) Application number: **20950415.8**

(22) Date of filing: **08.10.2020**

(51) International Patent Classification (IPC):
C09K 11/02 ^(2006.01) **C09K 11/88** ^(2006.01)
B82Y 20/00 ^(2011.01)

(52) Cooperative Patent Classification (CPC):
B82Y 20/00; B82Y 40/00; C09K 11/02; C09K 11/88

(86) International application number:
PCT/KR2020/095124

(87) International publication number:
WO 2022/039335 (24.02.2022 Gazette 2022/08)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

(30) Priority: **18.08.2020 KR 20200103430**

(71) Applicants:
• **Samsung Display Co., Ltd.**
Yongin-si, Gyeonggi-do 17113 (KR)
• **Research Business Foundation**
Sungkyunkwan University
Suwon-si, Gyeonggi-do 16419 (KR)

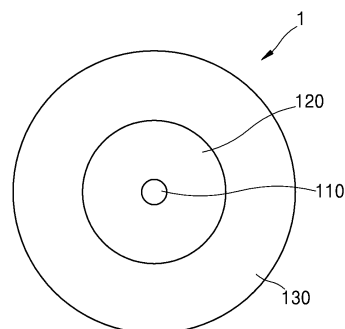
(72) Inventors:
• **KWON, Sun Young**
Yongin-Si Gyeonggi-do 17113 (KR)
• **BAE, Wan Ki**
Seoul 06592 (KR)
• **LEE, Hak June**
Suwon-Si Gyeonggi-do 16362 (KR)
• **KWON, Young Soo**
Yongin-Si Gyeonggi-do 17113 (KR)
• **OH, Keun Chan**
Yongin-Si Gyeonggi-do 17113 (KR)
• **LEE, Hyeok Jin**
Yongin-Si Gyeonggi-do 17113 (KR)
• **CHANG, Jun Hyuk**
Suwon-Si Gyeonggi-do 16361 (KR)

(74) Representative: **Marks & Clerk LLP**
15 Fetter Lane
London EC4A 1BW (GB)

(54) **SEMICONDUCTOR NANOPARTICLE AND ELECTRONIC DEVICE COMPRISING SAME**

(57) Provided are a semiconductor nanoparticle, an thin film including the same, and an electronic device including the thin film, the semiconductor nanoparticle including: a cluster consisting of a first semiconductor compound; a core covering at least a portion of the surface of the cluster and including a second semiconductor compound; and a shell covering at least a portion of the surface of the core and including a third semiconductor compound, wherein the first semiconductor compound and the third semiconductor compound each include zinc (Zn), the second semiconductor compound includes Zn, tellurium (Te), and selenium (Se), the first semiconductor compound and the second semiconductor compound are different from each other, and the second semiconductor compound and the third semiconductor compound are different from each other.

FIG. 1



EP 4 202 008 A1

Description

TECHNICAL FIELD

5 **[0001]** Provided are a semiconductor nanoparticle and an electronic device including the same.

BACKGROUND ART

10 **[0002]** Semiconductor nanoparticles, as nanoscale-sized crystalline materials with a size of several nanometers, exhibit a quantum confinement effect, and are also called quantum dots.

[0003] Semiconductor nanoparticles receive light from an excitation source and thus enter an excited state, and thereafter emit energy corresponding to an energy band gap. Semiconductor nanoparticles exhibit characteristics such as excellent color purity and high luminous efficiency, and accordingly, can be used in various applications. In detail, semiconductor nanoparticles may be used in a lighting apparatus, a display apparatus, and the like.

15

DESCRIPTION OF EMBODIMENTS

TECHNICAL PROBLEM

20 **[0004]** Provided are a semiconductor nanoparticle and an electronic device including the same. In detail, provided are a cadmium-free semiconductor nanoparticle and an electronic device including the same.

SOLUTION TO PROBLEM

25 **[0005]** According to an aspect, provided is a semiconductor nanoparticle including: a cluster consisting of a first semiconductor compound; a core covering at least a surface of the cluster and including a second semiconductor compound; and a shell covering at least a surface of the core and including a third semiconductor compound, wherein the first semiconductor compound and the third semiconductor compound each include zinc (Zn), the second semiconductor compound includes Zn, tellurium (Te), and selenium (Se), the first semiconductor compound and the second semiconductor compound are different from each other, and the second semiconductor compound and the third semiconductor compound are different from each other.

30

[0006] In an embodiment, the first semiconductor compound may include ZnSe.

[0007] In an embodiment, the second semiconductor compound may be represented by $\text{ZnSe}_{1-x}\text{Te}_x$, wherein x may satisfy $0.05 < x \leq 0.5$.

35

[0008] In an embodiment, x may satisfy $0.33 \leq x \leq 0.5$.

[0009] In an embodiment, the third semiconductor compound may include ZnSe or $\text{ZnSe}_y\text{S}_{1-y}$, wherein y may satisfy $0 \leq y < 1$.

[0010] In an embodiment, a band gap of the first semiconductor compound may be greater than that of the second semiconductor compound, and a band gap of the third semiconductor compound may be greater than that of the second semiconductor compound.

40

[0011] In an embodiment, the semiconductor nanoparticle may have a spherical quantum well.

[0012] In an embodiment, the semiconductor nanoparticle may emit light having a maximum emission wavelength in a range of about 445 nm to about 550 nm.

45

[0013] In an embodiment, the semiconductor nanoparticle may further include an outer shell that covers at least a surface of the shell and includes a fourth semiconductor compound, wherein the fourth semiconductor compound may include a Group II element.

[0014] In an embodiment, the fourth semiconductor compound may include Zn, and may be a binary compound or a ternary compound.

50

[0015] In an embodiment, the fourth semiconductor compound may include ZnS, ZnSe, ZnTe, ZnO, ZnSeS, ZnSeTe, ZnSTe, or any combination thereof.

[0016] In an embodiment, the semiconductor nanoparticle may emit light having a maximum emission wavelength in a range of about 470 nm to about 650 nm.

[0017] In an embodiment, the cluster may have an average diameter of less than or equal to about 0.5 nm.

[0018] In an embodiment, the core may have an average diameter in a range of about 2 nm to about 5 nm.

55

[0019] In an embodiment, the semiconductor nanoparticle may have an average diameter in a range of about 3 nm to about 13 nm.

[0020] According to another aspect, provided is an electronic device including: a first substrate; a light-emitting device; and a second substrate, wherein the second substrate may include the semiconductor nanoparticle.

[0021] In an embodiment, the semiconductor nanoparticle may be included in one region of the second substrate, and may absorb blue light and emit visible light.

[0022] In an embodiment, the second substrate may further include another region distinct from the one region, and the other region may include a scatterer but not include the semiconductor nanoparticle.

[0023] In an embodiment, the second substrate may be positioned in a traveling direction of light emitted from the light-emitting device.

[0024] According to another aspect, provided is an electronic device including: a first electrode; a second electrode; and an interlayer arranged between the first electrode and the second electrode, wherein the interlayer may include the semiconductor nanoparticle.

ADVANTAGEOUS EFFECTS OF DISCLOSURE

[0025] In the semiconductor nanoparticle, the lattice mismatch between the core and the shell may be reduced, thereby improving light efficiency. In addition, the semiconductor nanoparticle may have a larger diameter by being prepared using a cluster. Therefore, the electronic device including the semiconductor nanoparticle may have improved efficiency and improved color purity.

BRIEF DESCRIPTION OF DRAWINGS

[0026]

FIG. 1 is a schematic view of a semiconductor nanoparticle according to an embodiment.

FIG. 2 is a partially enlarged view of FIG. 1.

FIG. 3 is a schematic view of a semiconductor nanoparticle according to another embodiment.

FIG. 4 is a partially enlarged view of FIG. 3.

FIG. 5 is a diagram showing UV-Vis absorption spectra of Examples and Comparative Examples.

FIG. 6 is a diagram showing photoluminescence (PL) spectra of Examples and Comparative Examples.

FIG. 7 is a diagram showing PL quantum yield (QY) of Examples and Comparative Examples.

FIG. 8 is a diagram showing time-dependent PLQY of Examples and Comparative Examples.

FIG. 9 is a TEM image of Example 1, and FIG. 10 is a TEM image of Example 2.

FIGS. 11 and 12 are each a schematic cross-sectional view of a structure of an electronic device according to an embodiment.

MODE OF DISCLOSURE

[0027] As the disclosure may have diverse modified embodiments, embodiments are illustrated in the drawings and are described in the detailed description. An effect and a characteristic of the disclosure, and a method of accomplishing these will be apparent when referring to embodiments described with reference to the drawings. The disclosure may, however, be embodied in many different forms and should not be construed as limited to the embodiments set forth herein.

[0028] It will be understood that although the terms "first," "second," etc. used herein may be used herein to describe various components, these components should not be limited by these terms. These components are only used to distinguish one component from another.

[0029] An expression used in the singular encompasses the expression of the plural, unless it has a clearly different meaning in the context.

[0030] In the specification, it is to be understood that the terms such as "including," "having," and "comprising" are intended to indicate the existence of the features or components disclosed in the specification, and are not intended to preclude the possibility that one or more other features or components may exist or may be added. For example, unless otherwise limited, terms such as "including" or "having" may refer to either consisting of features or components described in the specification only or further including other components.

[0031] Like reference numerals in the drawings refer to like components, and the size of each component in the drawings may be exaggerated or reduced for clarity and convenience of description.

[0032] When a portion of a layer, film, region, plate, etc. is said to be "on" another portion, this includes not only the case in which the portion is "directly on" another portion, but also the case in which an intervening layer is placed therebetween. When a portion is placed "directly on" the other portion, this means that there is no intervening layer.

[0033] The term "maximum luminescence wavelength" used herein refers to a wavelength value corresponding to a point having a maximum emission intensity in a photoluminescence (PL) spectrum of a solution or film sample including a compound.

[0034] The term "full width at half maximum (FWHM)" used herein refers to a wavelength width at a point corresponding

to 1/2 of a maximum emission intensity in the above-described PL spectrum.

[0035] The term "Group" used herein refers to a group on the IUPAC Periodic Table of Elements.

[0036] The term "average diameter" used herein refers to an average value of diameters measured from all semiconductor nanoparticles included in any sample.

[0037] The term "average thickness" used herein refers to an average value of thicknesses measured from all semiconductor nanoparticles included in any sample.

[0038] Hereinafter, a semiconductor nanoparticle 1 according to an embodiment will be described with reference to FIGS. 1 and 2.

[0039] The semiconductor nanoparticle 1 includes a cluster 10 consisting of a first semiconductor compound, a core 120 covering at least a surface of the cluster 110 and including a second semiconductor compound, and a shell 130 covering at least a surface of the core 120 and including a third semiconductor compound.

[0040] When the core 120 included in the semiconductor nanoparticle 1 grows to cover at least a surface of the cluster 110, a lattice of the second semiconductor compound may be formed in the lattice shape of the first semiconductor compound. Then, the shell 130 may be formed to cover at least a surface of the core 120, and as a result, lattice mismatch between the core 120 and the shell 130 may be reduced. Accordingly, the semiconductor nanoparticle 1 may have improved luminescence efficiency.

[0041] The first semiconductor compound may include zinc (Zn).

[0042] In an embodiment, the semiconductor nanoparticle 1 may not include a heavy metal such as cadmium (Cd). Although the semiconductor nanoparticle 1 does not include a heavy metal such as Cd, the semiconductor nanoparticle 1 may have a spherical quantum well (SQW) structure by using Zn.

[0043] In an embodiment, the first semiconductor compound may include Zn together with one or more selected from Group VI elements.

[0044] In one or more embodiments, the first semiconductor compound may include Zn together with one or more selected from sulfur (S), selenium (Se) and tellurium (Te).

[0045] In an embodiment, the first semiconductor compound may be ZnSe.

[0046] In an embodiment, the cluster 110 may have an average diameter R_1 of less than or equal to about 1.5 nm. In one or more embodiments, the cluster 110 may have an average diameter R_1 of less than or equal to about 1.4 nm. Since the average diameter R_1 of the cluster 110 is less than or equal to about 1.5 nm, the cluster 110 is distinguished from a commonly mentioned core in the art. In addition, since the average diameter R_1 of the cluster 110 is less than or equal to about 1.5 nm, the cluster 110 may not satisfy a band gap suitable for luminescence. Typically, a core or the like may have a diameter in a range of about 2 nm to about 7 nm.

[0047] The second semiconductor compound may include Zn, Te, and Se.

[0048] In an embodiment, the second semiconductor compound may be represented by $\text{ZnSe}_{1-x}\text{Te}_x$, wherein x may satisfy $0.05 < x \leq 0.5$.

[0049] Here, x refers to a compositional ratio of Te to Zn in $\text{ZnSe}_{1-x}\text{Te}_x$ included in the core 120 of the semiconductor nanoparticle 1. In an embodiment, when x is satisfied within a range of greater than 0.05 and less than or equal to 0.5, the semiconductor nanoparticle 1 may emit visible light, for example, blue visible light or green visible light. In one or more embodiments, when x is less than or equal to 0.05, the proportion of Te in the core 120 of the semiconductor nanoparticle 1 decreases so that an emission wavelength of the semiconductor nanoparticle 1 is shortened. Thus, the semiconductor nanoparticle 1 may not emit visible light, or may emit purple visible light. In one or more embodiments, when x is less than or equal to 0.05, a thin film including the semiconductor nanoparticle 1 may have low absorbance for visible light, and thus an electronic device coupled with a light-emitting device emitting visible light may have reduced efficiency.

[0050] For example, x may satisfy $0.33 \leq x \leq 0.5$. When x satisfies $0.33 \leq x \leq 0.5$, the semiconductor nanoparticle 1 may emit green light.

[0051] In an embodiment, the core 120 may include two or more types of the second semiconductor compound having different compositions. For example, the core 120 may include $\text{ZnSe}_{0.75}\text{Te}_{0.25}$, $\text{ZnSe}_{0.66}\text{Te}_{0.33}$, $\text{ZnSe}_{0.50}\text{Te}_{0.50}$, or any combination thereof.

[0052] In an embodiment, the core 120 may have an average diameter R_2 in a range of about 2.0 nm to about 5.0 nm, for example, greater than or equal to 2.5 nm, greater than or equal to 3 nm, greater than or equal to 3.2 nm, less than or equal to 4.5 nm, or less than or equal to 4 nm.

[0053] The third semiconductor compound may include Zn.

[0054] In an embodiment, the third semiconductor compound may include Zn together with one or more selected from Group VI elements.

[0055] In one or more embodiments, the third semiconductor compound may include Zn together with one or more selected from S, Se, and Te.

[0056] In an embodiment, the third semiconductor compound may include ZnSe or $\text{ZnSe}_y\text{S}_{1-y}$, wherein y may satisfy $0 \leq y < 1$. Here, y refers to a compositional ratio of Se to Zn in $\text{ZnSe}_y\text{S}_{1-y}$. When the third semiconductor compound includes

ZnSe or $\text{ZnSe}_y\text{S}_{1-y}$, the lattice mismatch between the core 120 and the shell 130 may be reduced, thereby minimizing structural defects of nanoparticle. Accordingly, the shell may be formed to be sufficiently thick, so as to improve stability of the semiconductor nanoparticle.

[0057] For example, the third semiconductor compound may include ZnSe, ZnSeS, or ZnS.

[0058] In an embodiment, the shell may have an average thickness D_1 in a range of 0.25 nm to 1.5 nm, and for example, the average thickness D_1 of the shell may be greater than or equal to 0.3 nm, greater than or equal to 0.4 nm, greater than or equal to 0.5 nm, less than or equal to 1.3 nm, less than or equal to 1.2 nm, or less than or equal to 1.1 nm.

[0059] The shell 130 may act as a protective layer which prevents chemical denaturation of the core 120 to maintain semiconductor characteristics, and/or as a charging layer which imparts electrophoretic characteristics to the semiconductor nanoparticle.

[0060] The shell 130 may consist of a single layer or multiple layers, and an interface between the core 120 and the shell 130 may have a concentration gradient in which a concentration of an element present in the shell 130 decreases toward the center.

[0061] The first semiconductor compound and the second semiconductor compound may be different from each other, and the second semiconductor compound and the third semiconductor compound may be different from each other.

[0062] In an embodiment, the first semiconductor compound and the third semiconductor compound may be identical to each other.

[0063] For example, the first semiconductor compound may be ZnSe, and the third semiconductor compound may be also ZnSe, but embodiments are not limited thereto.

[0064] In an embodiment, a band gap of the cluster 110 may be greater than that of the core 120, and a band gap of the shell 130 may be also greater than that of the core 120.

[0065] For example, the band gap of the cluster 110 may be in a range of 3.7 eV to 3.72 eV, the band gap of the core 120 may be in a range of 2.4 eV to 2.95 eV, and the band of the shell 130 may be in a range of 2.82 eV to 3.2 eV, but embodiments are not limited thereto. When the above-described conditions are satisfied, the semiconductor nanoparticle 1 having improved efficiency and improved stability may be provided. In detail, when the band gaps are satisfied with the ranges above, the semiconductor nanoparticle having a Quasi-type II band structure, but having improved efficiency and improved stability may be provided.

[0066] In an embodiment, the semiconductor nanoparticle 1 may have a spherical quantum well (SQW).

[0067] The semiconductor nanoparticle 1 may emit visible light. For example, the semiconductor nanoparticle 1 may emit light having a maximum emission wavelength in a range of 445 nm to 550 nm. In an embodiment, the semiconductor nanoparticle 1 may emit light having a maximum emission wavelength in a range of 480 nm to 540 nm. In one or more embodiments, the semiconductor nanoparticle 1 may emit light having a maximum emission wavelength in a range of 530 nm to 540 nm. Accordingly, when the semiconductor nanoparticle 1 is applied to a color conversion member, blue or green color having high luminance and high color purity may be implemented.

[0068] In an embodiment, the semiconductor nanoparticle 1 may have an average diameter (R_2+2D_1) in a range of 3.0 nm to 13.0 nm. For example, the average diameter (R_2+2D_1) of the semiconductor nanoparticle 1 may be greater than or equal to 4.0 nm, greater than or equal to 4.5 nm, greater than or equal to 5.0 nm, less than or equal to 7.0 nm, less than or equal to 6.5 nm, or less than or equal to 6.0 nm.

[0069] In an embodiment, a full width at half maximum (FWHM) of an emission wavelength spectrum of the semiconductor nanoparticle 1 may be less than or equal to 60 nm, for example, less than or equal to 55 nm or less than or equal to 40 nm. When the FWHM of the emission wavelength spectrum of the semiconductor nanoparticle 1 is satisfied within the ranges above, the semiconductor nanoparticle 1 may have high color purity, excellent color reproducibility, and a wide viewing angle.

[0070] In an embodiment, the semiconductor nanoparticle 1 may have reduced lattice mismatch between the core 120 and the shell 130, and have reduced generation of structural defects at the interface between the core 120 and the shell 130, so that the shell 120 may be formed to a sufficient thickness. In one or more embodiments, as the semiconductor nanoparticle 1 is prepared by using the cluster 110, the semiconductor nanoparticle 1 may be prepared in a relatively large size. In this regard, the semiconductor nanoparticle according to an embodiment may implement high efficiency and high color purity.

[0071] In an embodiment, a form of the semiconductor nanoparticle 1 is not specifically limited, and may be any one commonly used in the art. For example, the semiconductor nanoparticle 1 may be a spherical, pyramidal, multi-arm, or cubic nanoparticle, nanotube, nanowire, nanofiber, or nanoplate particle.

[0072] In an embodiment, the semiconductor nanoparticle 1 may further include other compounds in addition to the above-described composition.

[0073] For example, the semiconductor nanoparticle 1 may include, in the core 120 or the shell 130, a Group II-VI compound, a Group III-VI compound, a Group III-V compound, a Group IV-VI compound, a Group IV element or compound, a Group I-III-VI compound, or a combination thereof.

[0074] For example, the Group II-VI compound may include: a binary compound selected from CdS, CdSe, CdTe,

ZnS, ZnSe, ZnTe, ZnO, HgS, HgSe, HgTe, MgSe, MgS, and a mixture thereof; a ternary compound selected from CdSeS, CdSeTe, CdSTe, ZnSeS, ZnSeTe, ZnSTe, HgSeS, HgSeTe, HgSTe, CdZnS, CdZnSe, CdZnTe, CdHgS, CdHgSe, CdHgTe, HgZnS, HgZnSe, HgZnTe, MgZnSe, MgZnS, and a mixture thereof; a quaternary compound selected from CdZnSeS, CdZnSeTe, CdZnSTe, CdHgSeS, CdHgSeTe, CdHgSTe, HgZnSeS, HgZnSeTe, HgZnSTe, and a mixture thereof; or any combination thereof.

[0075] For example, The Group III-VI compound may include: a binary compound selected from In_2S_3 , In_2Se_3 , and a mixture thereof; a ternary compound selected from InGaS_3 , InGaSe_3 , and a mixture thereof; or any combination thereof.

[0076] For example, the Group III-V compound may include: a binary compound selected from GaN, GaP, GaAs, GaSb, AlN, AlP, AlAs, AlSb, InN, InP, InAs, InSb, and a mixture thereof; a ternary compound selected from GaNP, GaNAS, GaNSb, GaPAs, GaPSb, AlNP, AlNAs, AlNSb, AlPAs, AlPSb, InGaP, InAlP, InNP, InNAs, InNSb, InPAs, InPSb, and a mixture thereof; a quaternary compound selected from GaAlNP, GaAlNAs, GaAlNSb, GaAlPAs, GaAlPSb, GaInNP, GaInNAs, GaInNSb, GaInPAs, GaInPSb, InAlNP, InAlNAs, InAlNSb, InAlPAs, InAlPSb, and a mixture thereof; or any combination thereof. The Group III-V semiconductor compound may further include a Group II metal (for example, InZnP, etc.).

[0077] For example, the Group IV-VI compound may include: a binary compound selected from SnS, SnSe, SnTe, PbS, PbSe, PbTe, and a mixture thereof; a ternary compound selected from SnSeS, SnSeTe, SnSTe, PbSeS, PbSeTe, PbSTe, SnPbS, SnPbSe, SnPbTe, and a mixture thereof; a quaternary compound selected from SnPbSSe, SnPbSeTe, SnPbSTe, and a mixture thereof; or any combination thereof.

[0078] For example, The Group IV element or compound may include: a single element compound selected from Si, Ge, and a mixture thereof; a binary compound selected from SiC, SiGe, and a mixture thereof; or any combination thereof.

[0079] For example, the Group I-III-VI semiconductor compound may include a ternary compound selected from AgInS, AgInS₂, CuInS, CuInS₂, CuGaO₂, AgGaO₂, AgAlO₂, and a mixture thereof; or any combination thereof.

[0080] The binary compound, the ternary compound, or the quaternary compound may exist in particles at uniform concentration, or may exist in the same particle in a state in which a concentration distribution is partially different.

[0081] In an embodiment, the shell 130 may further include an metal oxide, a non-metal oxide, or a combination thereof.

[0082] For example, the metal oxide or the non-metal oxide may be: a binary compound, such as SiO₂, Al₂O₃, TiO₂, ZnO, MnO, Mn₂O₃, Mn₃O₄, CuO, FeO, Fe₂O₃, Fe₃O₄, CoO, Co₃O₄, NiO, and the like; or a ternary compound, such as MgAl₂O₄, CoFe₂O₄, NiFe₂O₄, CoMn₂O₄, and the like.

[0083] Hereinafter, a semiconductor nanoparticle 2 according to another embodiment will be described with reference to FIGS. 3 and 4.

[0084] The semiconductor nanoparticle 2 includes: a cluster 210 consisting of a first semiconductor compound; a core 220 covering at least a surface of the cluster 210 and including a second semiconductor compound; a first shell 230 covering at least a surface of the core 220 and including a third semiconductor compound; and a second shell 240 covering at least a surface of the first shell 230 and including a fourth semiconductor compound. Here, the first shell 230 and the second shell 240 may be referred to as an inner shell and an outer shell, respectively. The descriptions of the first semiconductor compound, the second semiconductor compound, and the third semiconductor compound included in the semiconductor nanoparticle 2 may be referred to those described in connection with FIGS. 1 and 2, and may be the same as the first semiconductor compound, the second semiconductor compound, and the third semiconductor compound included in the semiconductor nanoparticle 1, respectively. Thus, overlapping descriptions will be omitted.

[0085] The fourth semiconductor compound may include a Group II element.

[0086] In an embodiment, the fourth semiconductor compound may include Zn, and may be a binary compound or a ternary compound.

[0087] In one or more embodiments, the fourth semiconductor compound may include ZnS, ZnSe, ZnTe, ZnO, ZnSeS, ZnSeTe, or ZnSTe.

[0088] In one or more embodiments, the first semiconductor compound may be ZnS.

[0089] In an embodiment, the outer shell may have an average thickness D_2 in a range of 0.3 nm to 1.5 nm. For example, the average thickness D_2 of the outer shell may be greater than or equal to 0.4 nm, greater than or equal to 0.5 nm, less than or equal to 1.4 nm, less than or equal to 1.3 nm, less than or equal to 1.2 nm, or less than or equal to 1.1 nm.

[0090] The outer shell 240 may act as a protective layer which prevents chemical denaturation of the core 220 to maintain semiconductor characteristics, and/or as a charging layer which imparts electrophoretic characteristics to the semiconductor nanoparticle 2.

[0091] The outer shell 240 may consist of a single layer or multiple layers, and an interface between the shell 230 and the outer shell 240 may have a concentration gradient in which a concentration of an element present in the outer shell 240 decreases toward the center.

[0092] The semiconductor nanoparticle 2 may emit visible light other than blue light. The semiconductor nanoparticle 2 may emit light having a maximum emission wavelength in a range of 470 nm to 650 nm. In an embodiment, the semiconductor nanoparticle 2 may emit light having a maximum emission wavelength in a range of 490 nm to 570 nm.

Accordingly, when the semiconductor nanoparticle 2 is applied to a color conversion member, green color having high luminance and high color purity may be implemented.

[0093] In an embodiment, the semiconductor nanoparticle 2 may have an average diameter ($R_2+2D_1+2D_2$) in a range of 3.0 nm to 13.0 nm. For example, the average diameter $R_2+2D_1+2D_2$ of the semiconductor nanoparticle 2 may be greater than or equal to 4.0 nm, greater than or equal to 4.5 nm, greater than or equal to 5.0 nm, greater than or equal to 5.5 nm, greater than or equal to 6.0 nm, less than or equal to 10.0 nm, less than or equal to 9.5 nm, less than or equal to 9.0 nm, less than or equal to 8.5 nm, or less than or equal to 8.0 nm.

[0094] In an embodiment, an FWHM of an emission wavelength spectrum of the semiconductor nanoparticle 2 may be less than or equal to 60 nm, for example, less than or equal to 55 nm or less than or equal to 40 nm. When the FWHM of the emission wavelength spectrum of the semiconductor nanoparticle 2 is satisfied within the ranges above, the semiconductor nanoparticle 2 may have high color purity, excellent color reproducibility, and a wide viewing angle.

[0095] Hereinafter, an electronic device including the above-described semiconductor nanoparticle will be described.

[0096] The electronic device may include a light-emitting device including: the semiconductor nanoparticle and a first electrode; a second electrode; and an interlayer arranged between the first electrode and the second electrode.

[0097] In an embodiment, the electronic device may include a liquid crystal display apparatus, an organic light-emitting display apparatus, or an inorganic light-emitting display apparatus.

[0098] For example, when the electronic device further includes a liquid crystal, the electronic device may be a liquid crystal display apparatus. Here, the light-emitting device may act as a light source, and the semiconductor nanoparticle may be included outside the light-emitting device and the liquid crystal to act as a color conversion member.

[0099] In an embodiment, in the case where the interlayer of the light-emitting device includes an emission layer and the emission layer includes an organic material, the electronic device may be an organic light-emitting display device. Here, the light-emitting device may act as a light source, and the semiconductor nanoparticle may be included outside the light-emitting device to act as a color conversion member.

[0100] In one or more embodiments, in the case where the interlayer of the light-emitting device includes an emission layer and the emission layer includes an inorganic material such as the semiconductor nanoparticle, the electronic device may be an inorganic light-emitting display device.

[0101] The electronic device may further include a thin-film transistor in addition to the light-emitting device as described above. The thin-film transistor may include a source electrode, a drain electrode, and an activation layer, wherein any one of the source electrode and the drain electrode may be electrically connected to any one of the first electrode and the second electrode of the light-emitting device.

[0102] The thin-film transistor may further include a gate electrode, a gate insulating layer, and the like.

[0103] The active layer may include crystalline silicon, amorphous silicon, an organic semiconductor, an oxide semiconductor, and the like.

[0104] The electronic device may further include a sealing portion for sealing the light-emitting device. The sealing portion allows light from the light-emitting device to be extracted to the outside, and simultaneously prevents ambient air and moisture from penetrating into the light-emitting device. The sealing portion may be a sealing substrate including a transparent glass substrate or a plastic substrate. The sealing portion may be a thin-film encapsulation layer including at least one layer of an organic layer and/or an inorganic layer. When the sealing portion is a thin film encapsulation layer, the electronic device may be flexible.

[0105] Various functional layers may be additionally located on the sealing portion according to the use of the electronic device. Examples of the functional layer are a color filter, a color conversion layer, a touch screen layer, and a polarizing layer. The touch screen layer may be a pressure-sensitive touch screen layer, a capacitive touch screen layer, or an infrared touch screen layer.

[0106] Hereinafter, an electronic device 3 according to an embodiment will be described in detail with reference to FIG. 11.

[0107] The electronic device 3 may include a first substrate 310, a light-emitting device 320, and a second substrate 340.

[0108] The semiconductor nanoparticle may be included outside the light-emitting device 320 (i.e., on a first electrode and/or a second electrode). In detail, the semiconductor nanoparticle may be included in the second substrate 340 located outside the light-emitting device 320. The second substrate 340 may function as a color conversion member, and the light-emitting device 320 may function as a light source.

[0109] The light-emitting device 320 may include a first electrode 321, a second electrode 323, and an interlayer 322 arranged between the first electrode 321 and the second electrode 323.

[0110] The electronic device 3 may be an organic light-emitting display device. Accordingly, the light-emitting device 320 may include an organic emission layer in the interlayer 322.

[0111] A pixel-defining layer 330 may be arranged on the first electrode 321. The pixel-defining layer 330 exposes a region of the first electrode 321, and the interlayer 322 may be arranged in the exposed region.

[0112] In an embodiment, a region 342 of the second substrate 340 may include the semiconductor nanoparticle. In this case, the second substrate 340 may be positioned in a direction which light emitted from the light-emitting device

320 travels.

[0113] The semiconductor nanoparticle may absorb blue light and emit visible light. Accordingly, the second substrate 340 may be designed to absorb blue light and emit light having a wide color range of wavelengths. Accordingly, the light-emitting device 320 may emit blue light having, for example, a maximum emission wavelength in a range of 400 nm to 490 nm, and the thin film may absorb the blue light and emit visible light having, for example, a maximum emission wavelength in a range of 445 nm to 650 nm.

[0114] In an embodiment, the second substrate 340 may further include a scatterer.

[0115] In an embodiment, the second substrate 340 may further include another region (not shown) different from the region 341, and the other region may not include the semiconductor nanoparticle, and the other region may transmit the blue light from the light-emitting device 320. In detail, only the region 341 may include the semiconductor nanoparticle, and the other region may include only the scatterer.

[0116] In an embodiment, the second substrate 340 may further include a lightshielding pattern 344 between the region 341 and the other region.

[0117] Hereinafter, an electronic device 4 according to another embodiment will be described in detail with reference to FIG. 12.

[0118] The electronic device 4 includes a first substrate 410 and a light-emitting device 420.

[0119] The light-emitting device 420 includes a first electrode 421, a second electrode 423, and an interlayer 422 arranged between the first electrode 421 and the second electrode 423.

[0120] The semiconductor nanoparticle may be included in the interlayer 422, for example, in an emission layer included in the interlayer 422.

[0121] The semiconductor nanoparticle may emit visible light. Accordingly, the light-emitting device 420 may be designed to emit light having a wide color range of wavelengths. For example, the semiconductor nanoparticle may emit visible light having a maximum emission wavelength in a range of 445 nm to 650 nm.

[0122] The interlayer 422 may further include an auxiliary layer between the emission layer and the first electrode 421 and/or between the emission layer and the second electrode 423. The auxiliary layer may directly contact the emission layer. The auxiliary layer may improve thin film characteristics of the emission layer.

[0123] The interlayer 422 may further include a first charge transport region between the emission layer and the first electrode 421 and/or a second charge transport region between the emission layer and the second electrode 423.

[0124] Hereinafter, a method of preparing the semiconductor nanoparticle will be described in detail.

[0125] The method of preparing the semiconductor nanoparticle includes: forming a cluster consisting of a first semiconductor compound and then forming a core including a second semiconductor compound to cover at least a surface of the cluster; and forming a shell including a third semiconductor compound to cover at least a surface of the core.

[0126] The first semiconductor compound and the third semiconductor compound each include Zn, and the second semiconductor compound includes Zn, Te, and Se. The first semiconductor compound and the second semiconductor compound may be different from each other, and the second semiconductor compound and the third semiconductor compound may be different from each other.

[0127] In an embodiment, a mixture of a precursor of the first semiconductor compound and a solvent may be reacted at a cluster-forming temperature, for example, a temperature in a range of 200 °C to 250 °C, for example 230 °C to form a cluster consisting of the first semiconductor compound. The precursor of the first semiconductor compound essentially includes Zn.

[0128] The cluster thus formed does not undergo any separate isolation process, and a Se precursor and/or a Te precursor may be directly added thereto to form a core including the second semiconductor compound.

[0129] Since the cluster thus formed does not undergo any separate isolation process, a core that covers at least a portion of the cluster may be formed right on top of the cluster after the cluster grows. Accordingly, the core may grow along the lattice of the cluster. For example, when the cluster undergoes an isolation process, the highly reactive Se precursor and/or Te precursor may react with Zn to form a core that does not include the cluster, rather than a core that covers at least a portion of the cluster. That is, when the cluster includes Cd, due to a large difference of reactivity to Zn, a core may not be formed according to the method described above.

[0130] Instead, after the Se precursor and/or the Te precursor is added to the cluster, a resultant mixture may be allowed for a reaction at a temperature in a range of 200 °C to 250 °C, for example, at a temperature of 230 °C. For example, after the Se precursor and/or the Te precursor is immediately added to the mixture of precursor of the first semiconductor compound and the solvent, the reaction may proceed for 30 minutes to form a core.

[0131] Next, a precursor of the third semiconductor compound may be added and reacted to form a shell. In an embodiment, a reaction temperature at which the shell is formed may be in a range of 280 °C to 320 °C, for example, 300 °C to 320 °C, and a reaction time for which the shell is formed is 15 minutes.

[0132] In an embodiment, following the forming of the core, a purification process and/or a separation process or may be further performed or may be omitted.

[0133] In an embodiment, the solvent may be an organic solvent. For example, the solvent may be trioctylamine,

oleylamine, 1-octadecene (ODE), or the like.

[0134] Other details on the method of preparing the semiconductor nanoparticle will be understood by a person skilled in the art with reference to examples to be described later.

[0135] Hereinafter, semiconductor nanoparticles according to examples will be described in more detail.

[Examples]

Example 1: Synthesis of ZnSe/ZeSe_{0.66}Te_{0.33}/ZnSe semiconductor nanoparticle

[0136] In a three-necked flask, 0.6 mmol of zinc oleate and 10 mL of 1-ODE were added. 0.2 mmol of diphenylphosphine selenide was added thereto at 230 °C, and then right after, 0.1 mmol of trioctylphosphine telluride was added. The mixture was allowed to reaction for 30 minutes.

[0137] Next, 1 mmol of zinc oleate and 1 mmol of trioctylphosphine selenide were added thereto and then allowed to react for 15 minutes at a temperature raised to 300 °C, thereby forming a zinc selenide shell and a semiconductor nanoparticle of Example 1.

[0138] The semiconductor nanoparticle of Example 1 included a ZnSe cluster, a ZeSe_{0.66}Te_{0.33} core, and a ZnSe shell. FIG. 9 shows a TEM image of the semiconductor nanoparticle of Example 1.

Example 2: Synthesis of ZnSe/ZeSe_{0.66}Te_{0.33}/ZnSe/ZnS semiconductor nanoparticle

[0139] In a three-necked flask, 0.6 mmol of zinc oleate and 10 mL of 1-ODE were added. 0.2 mmol of diphenylphosphine selenide was added thereto at 230 °C, and then, right after 0.1 mmol of trioctylphosphine telluride was added. The mixture was allowed to react for 30 minutes.

[0140] Next, 1 mmol of zinc oleate and 1 mmol of trioctylphosphine selenide were added thereto and then allowed to react for 15 minutes at a temperature raised to 300 °C, thereby forming a zinc selenide shell.

[0141] Then, 2 mmol zinc oleate and 2 mmol trioctylphosphine sulfide were added thereto and reacted for 1 hour to form a zinc sulfide shell to obtain a semiconductor nanoparticle of Example 2.

[0142] The semiconductor nanoparticle of Example 2 included a ZnSe cluster, a ZeSe_{0.66}Te_{0.33} core, a ZnSe shell, and a ZnS outer shell. FIG. 10 shows a TEM image of the semiconductor nanoparticle of Example 2.

Comparative Example 1: Synthesis of ZeSe_{0.66}Te_{0.33}/ZnSe semiconductor nanoparticle

[0143] In a three-necked flask, 0.6 mmol of zinc oleate, 0.2 mmol of diphenylphosphine selenide, 0.1 mmol of trioctylphosphine telluride, and 10 mL of 1-ODE were added at the same time and allowed to reaction at 230 °C for 30 minutes.

[0144] Next, 1 mmol of zinc oleate and 1 mmol of trioctylphosphine selenide were added thereto and then allowed to react for 15 minutes at a temperature raised to 300 °C, thereby forming a zinc selenide shell and a semiconductor nanoparticle of Comparative Example 1.

Comparative Example 2: Synthesis of ZeSe_{0.66}Te_{0.33}/ZnSe/ZnS semiconductor nanoparticle

[0145] In a three-necked flask, 0.6 mmol of zinc oleate, 0.2 mmol of diphenylphosphine selenide, 0.1 mmol of trioctylphosphine telluride, and 10 mL of 1-ODE were added at the same time and allowed to reaction at 230 °C for 30 minutes.

[0146] Next, 1 mmol of zinc oleate and 1 mmol of trioctylphosphine selenide were added thereto and then allowed to react for 15 minutes at a temperature raised to 300 °C, thereby forming a zinc selenide shell.

[0147] Then, 2 mmol zinc oleate and 2 mmol trioctylphosphine sulfide were added thereto and reacted for 1 hour to form a zinc sulfide shell to obtain a semiconductor nanoparticle of Comparative Example 2.

Comparative Example 3: Synthesis of ZnSe/ZeSe_{0.66}Te_{0.33} semiconductor nanoparticle

[0148] In a three-necked flask, 0.6 mmol of zinc oleate and 10 mL of 1-ODE were added. 0.2 mmol of diphenylphosphine selenide was added thereto at 230 °C, and then, right after 0.1 mmol of trioctylphosphine telluride was added. The mixture was allowed to react for 30 minutes at 230 °C to obtain a semiconductor nanoparticle of Comparative Example 3.

Comparative Example 4: Synthesis of ZnSe semiconductor nanoparticle

[0149] In a three-necked flask, 0.6 mmol of zinc oleate and 10 mL of 1-ODE were added. 0.2 mmol of diphenylphosphine selenide was added thereto at 230 °C. The mixture was allowed to react for 30 minutes at a temperature raised to 300 °C to obtain a semiconductor nanoparticle of Comparative Example 4.

Evaluation Example 1

[0150] Each of the semiconductor nanoparticles of Examples 1 and 2 and Comparative Examples 1 to 4 was evaluated in terms of a UV-Vis spectrum, a PL spectrum, a maximum emission wavelength, an FWHM, and a PLQY, and results thereof are shown in Table 1 and FIGS. 5 to 8. Here, the PLQY was measured by dispersing the semiconductor nanoparticles in toluene and adjusting absorbance to be 0.1 at 450 nm.

Table 1

	Semiconductor nanoparticle	Maximum emission wavelength (nm)	FWHM (nm)	PLQY (%)
Exempl e 1	ZnSe/ZeSe _{0.66} Te _{0.33} /ZnSe	510	41	85
Exempl e 2	ZnSe/ZeSe _{0.66} Te _{0.33} /ZnSe/ZnS	525	45	95
Compar ative Exempl e 1	ZeSe _{0.66} Te _{0.33} /ZnSe	508	47	55
Compar ative Exempl e 2	ZeSe _{0.66} Te _{0.33} /ZnSe/ZnS	520	51	65
Compar ative Exempl e 3	ZnSe/ZeSe _{0.66} Te _{0.33}	491	42	75
Compar ative Exempl e 4	ZnSe	430	22	70

[0151] Referring to Table 1, it was confirmed that the semiconductor nanoparticles of Examples 1 and 2 had a narrow FWHM and an excellent PLQY.

[0152] In addition, referring to Table 1 and FIG. 6, it was confirmed that, unlike the semiconductor nanoparticles of Examples 1 and 2 that emitted green light, the semiconductor nanoparticles of Comparative Examples 3 and 4 emitted visible light having a maximum emission wavelength of less than 500 nm.

[0153] Referring to FIG. 5, it was confirmed that the semiconductor nanoparticles of Examples 1 and 2 had high absorbance for blue light compared to the semiconductor nanoparticles of Comparative Examples 3 and 4.

[0154] Referring to Table 1 and FIG. 7, it was confirmed that the semiconductor nanoparticle of Example 2 including the cluster had a significantly improved PLQY compared to the semiconductor nanoparticle of Comparative Example 2 not including the cluster.

[0155] Referring to FIG. 8, it was confirmed that the semiconductor nanoparticle of Example 2 including the cluster had a significantly longer lifespan than the semiconductor nanoparticle of Comparative Example 2 not including the cluster.

Claims

1. A semiconductor nanoparticle comprising:

a cluster consisting of a first semiconductor compound;
 a core covering at least a surface of the cluster and comprising a second semiconductor compound; and
 a shell covering at least a surface of the core and comprising a third semiconductor compound,
 wherein the first semiconductor compound and the third semiconductor compound each comprise zinc (Zn),
 the second semiconductor compound comprises Zn, tellurium (Te), and selenium (Se),
 the first semiconductor compound and the second semiconductor compound are different from each other, and
 the second semiconductor compound and the third semiconductor compound are different from each other.

2. The semiconductor nanoparticle of claim 1, wherein the first semiconductor compound comprises ZnSe.

3. The semiconductor nanoparticle of claim 1, wherein the second semiconductor compound is represented by ZnSe_{1-x}Te_x, and x satisfies 0.05 < x ≤ 0.5.

4. The semiconductor particle of claim 3, wherein x satisfies $0.33 \leq x \leq 0.5$.
5. The semiconductor nanoparticle of claim 1, wherein the third semiconductor compound comprises ZnSe or $\text{ZnSe}_y\text{S}_{1-y}$, and y satisfies $0 \leq y < 1$.
6. The semiconductor nanoparticle of claim 1, wherein a band gap of the cluster is greater than that of the core, and a band gap of the shell is greater than that of the core.
7. The semiconductor nanoparticle of claim 1, wherein the semiconductor nanoparticle has a spherical quantum well.
8. The semiconductor nanoparticle of claim 1, wherein the semiconductor nanoparticle emits light having a maximum emission wavelength in a range of 445 nm to 550 nm.
9. The semiconductor nanoparticle of claim 1, further comprising an outer shell covering at least a surface of the shell and comprising a fourth semiconductor compound, wherein the fourth semiconductor compound comprises a Group II element.
10. The semiconductor nanoparticle of claim 9, wherein the fourth semiconductor comprises Zn, and is a binary compound or a ternary compound.
11. The semiconductor nanoparticle of claim 9, wherein the fourth semiconductor compound comprises ZnS, ZnSe, ZnTe, ZnO, ZnSeS, ZnSeTe, ZnSTe, or any combination thereof.
12. The semiconductor nanoparticle of claim 9, wherein the semiconductor nanoparticle emits light having a maximum emission wavelength in a range of 470 nm to 650 nm.
13. The semiconductor nanoparticle of claim 1, wherein an average diameter of the cluster is less than or equal to 1.5 nm.
14. The semiconductor nanoparticle of claim 1, wherein an average diameter of the core is in a range of 2.0 nm to 5.0 nm.
15. The semiconductor nanoparticle of claim 1, wherein an average diameter of the semiconductor nanoparticle is in a range of 3.0 nm to 13.0 nm.
16. An electronic device comprising a first substrate, a light-emitting device, and a second substrate, wherein the second substrate comprises the semiconductor nanoparticle according to any one of claims 1 to 15.
17. The electronic device of claim 16, wherein the semiconductor nanoparticle is comprised in one region of the second substrate, and the semiconductor nanoparticle absorbs blue light and emits visible light.
18. The electronic device of claim 17, wherein the second substrate further includes another region distinct from the one region, and the other region comprises a scatterer, but does not comprise the semiconductor nanoparticle.
19. The electronic device of claim 16, wherein the second substrate is positioned in a direction in which light emitted from the light-emitting device travels.
20. An electronic device comprising a first electrode, a second electrode, and an interlayer between the first electrode and the second electrode, wherein the interlayer comprises the semiconductor nanoparticle according to any one of claims 1 to 15.

FIG. 1

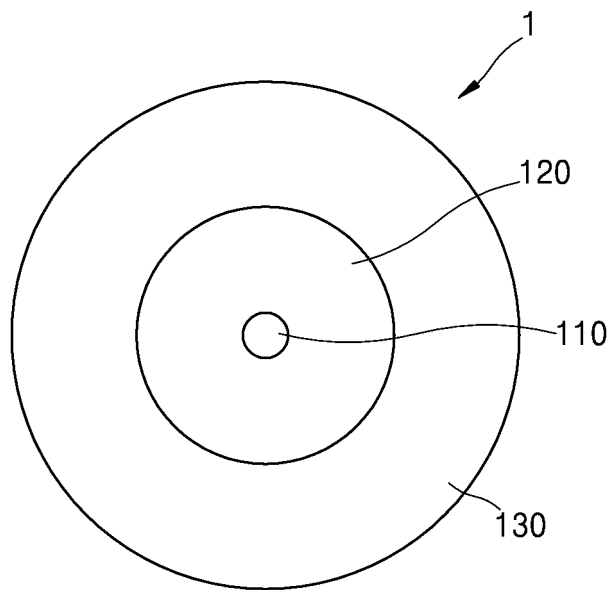


FIG. 2

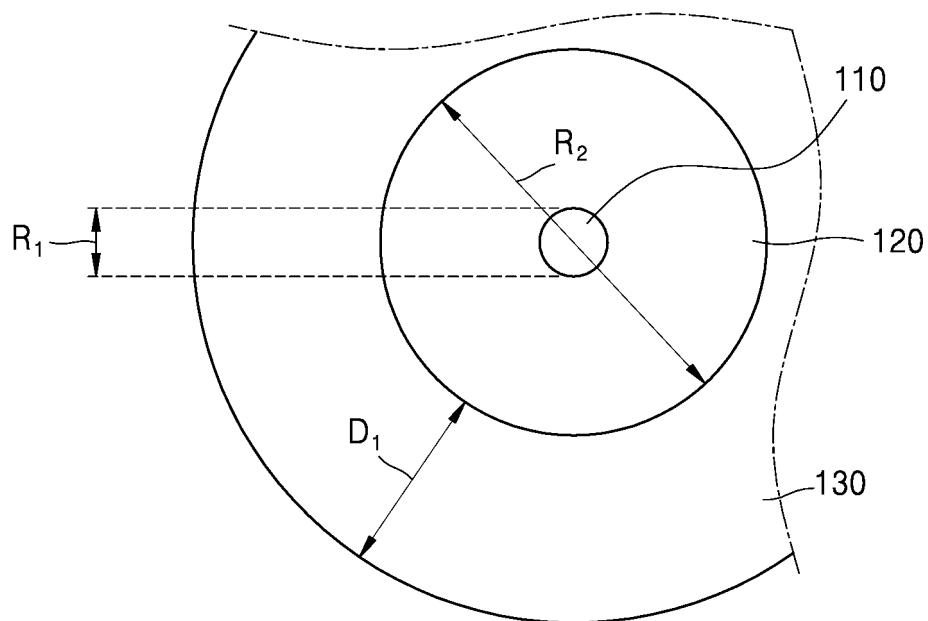


FIG. 3

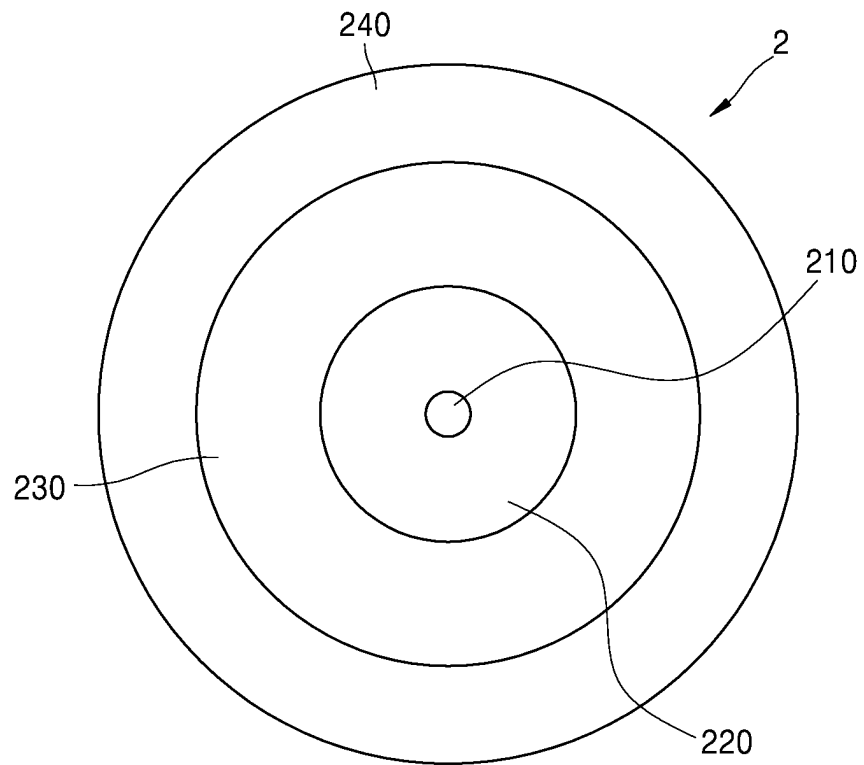


FIG. 4

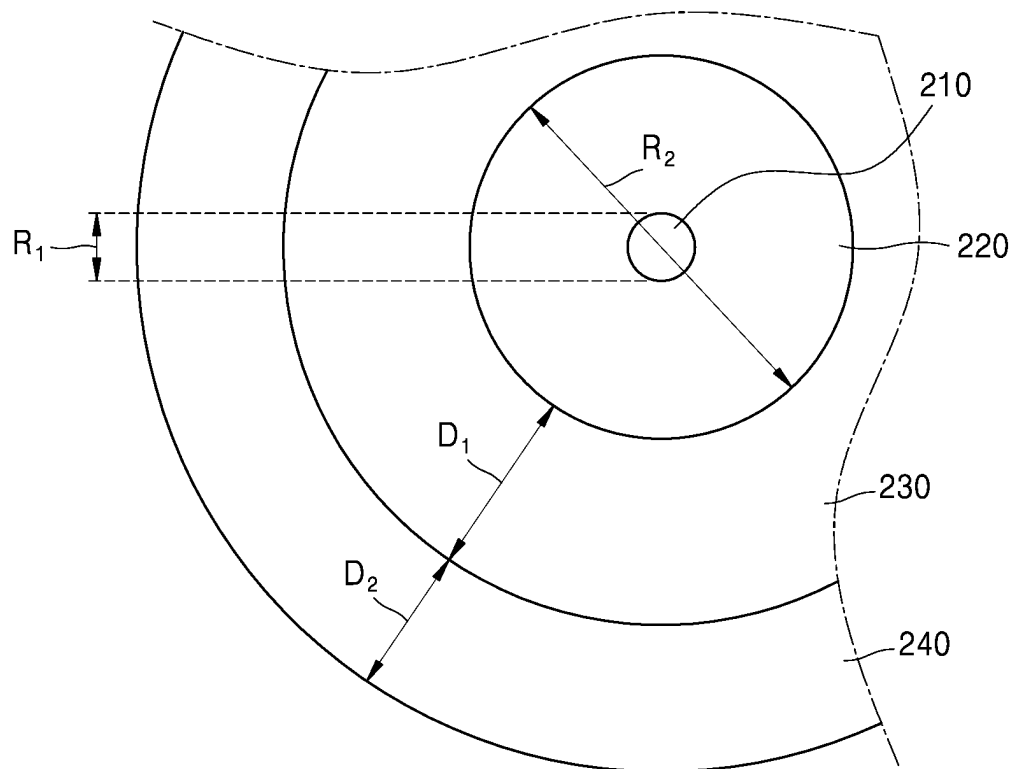


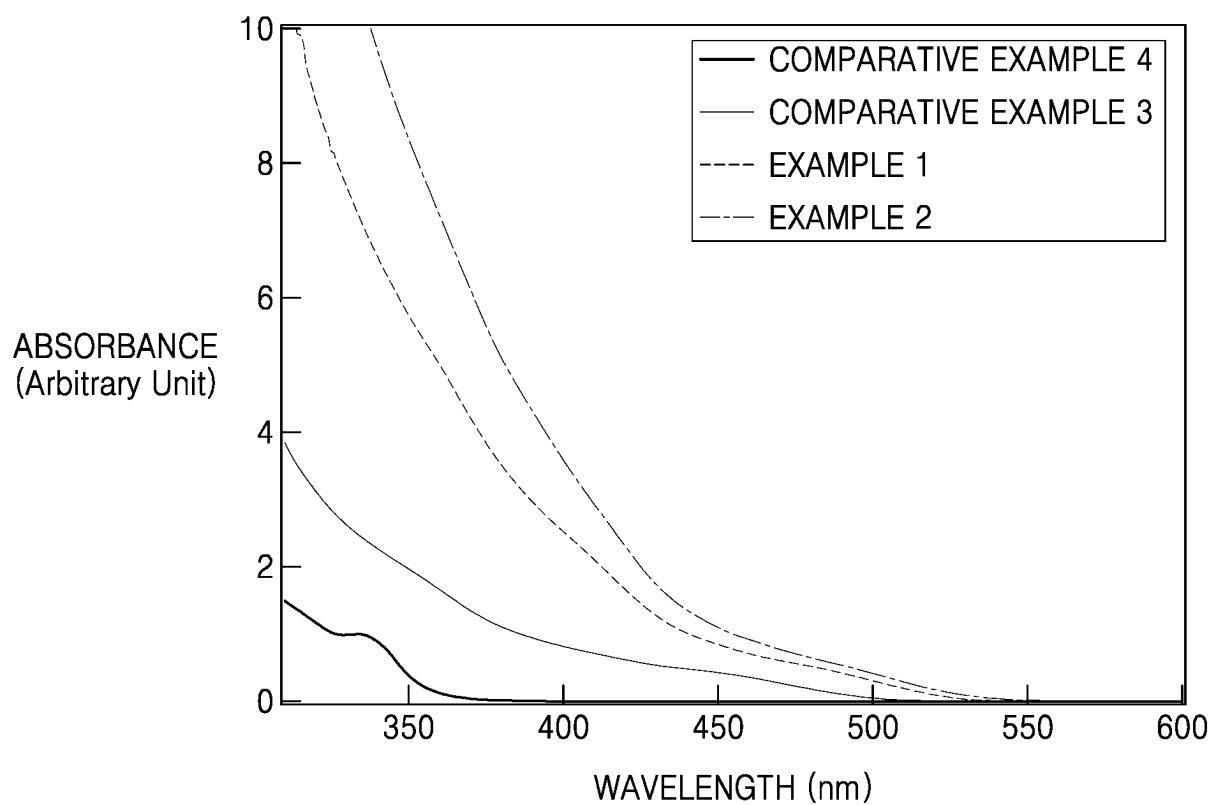
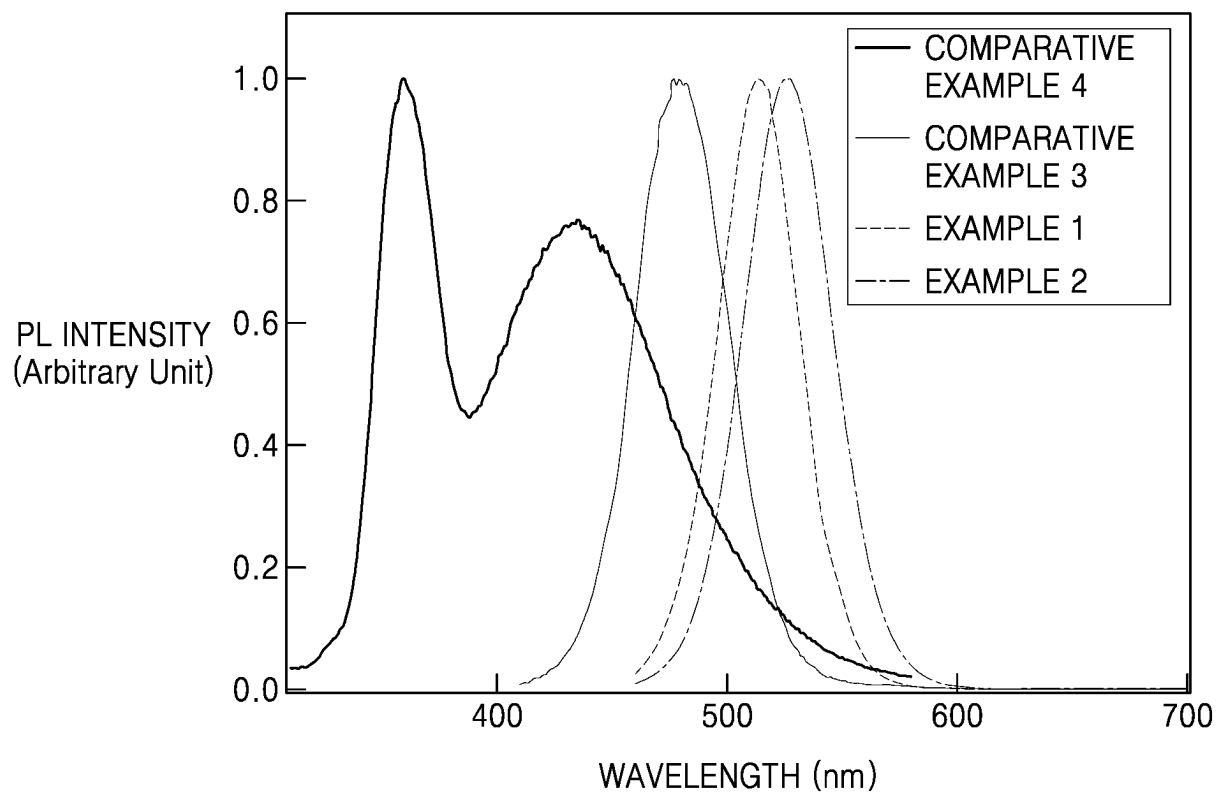
FIG. 5**FIG. 6**

FIG. 7

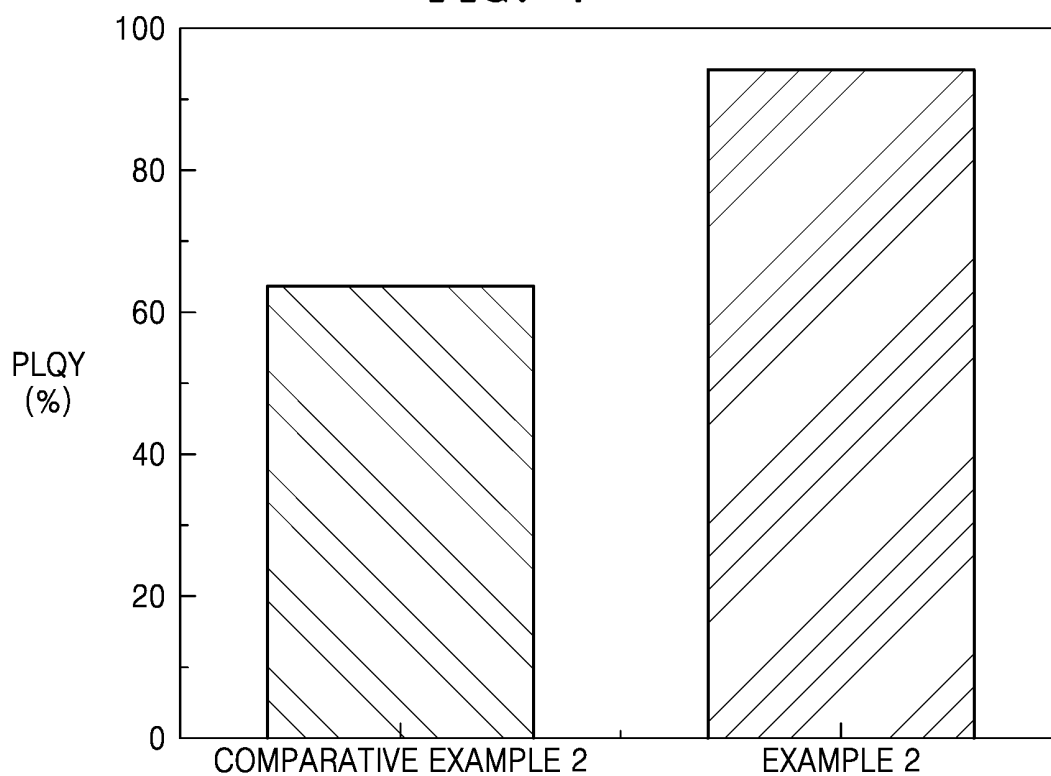


FIG. 8

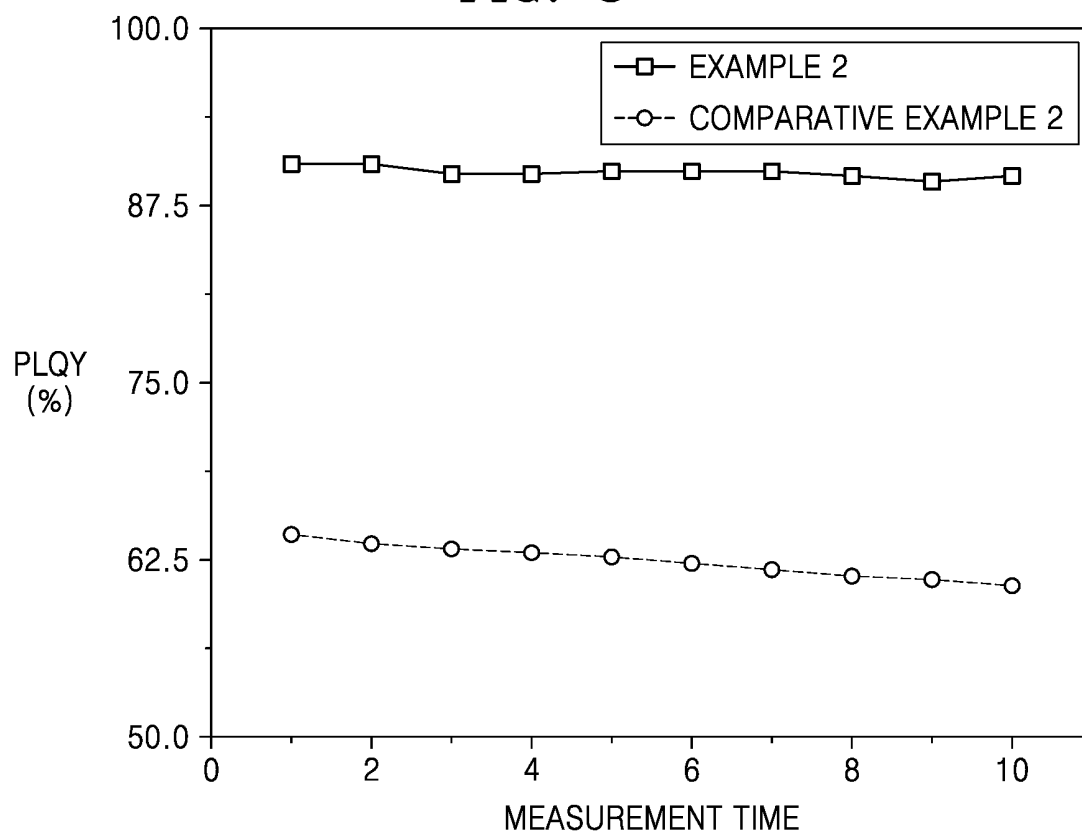


FIG. 9

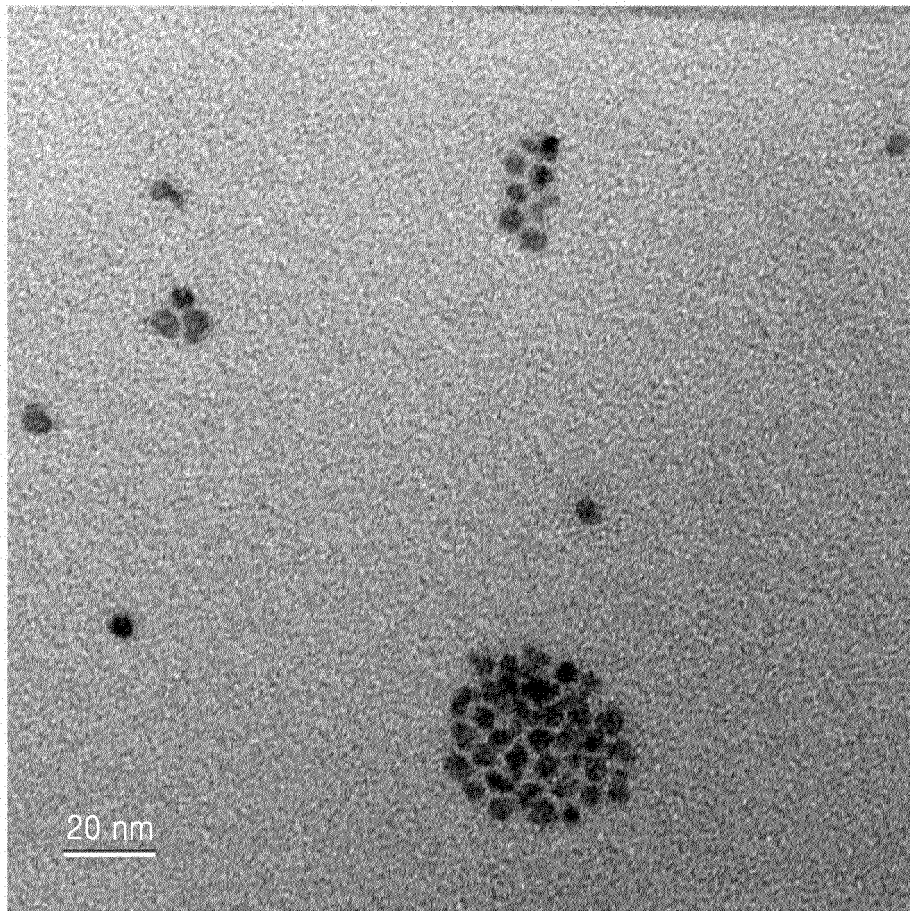


FIG. 10

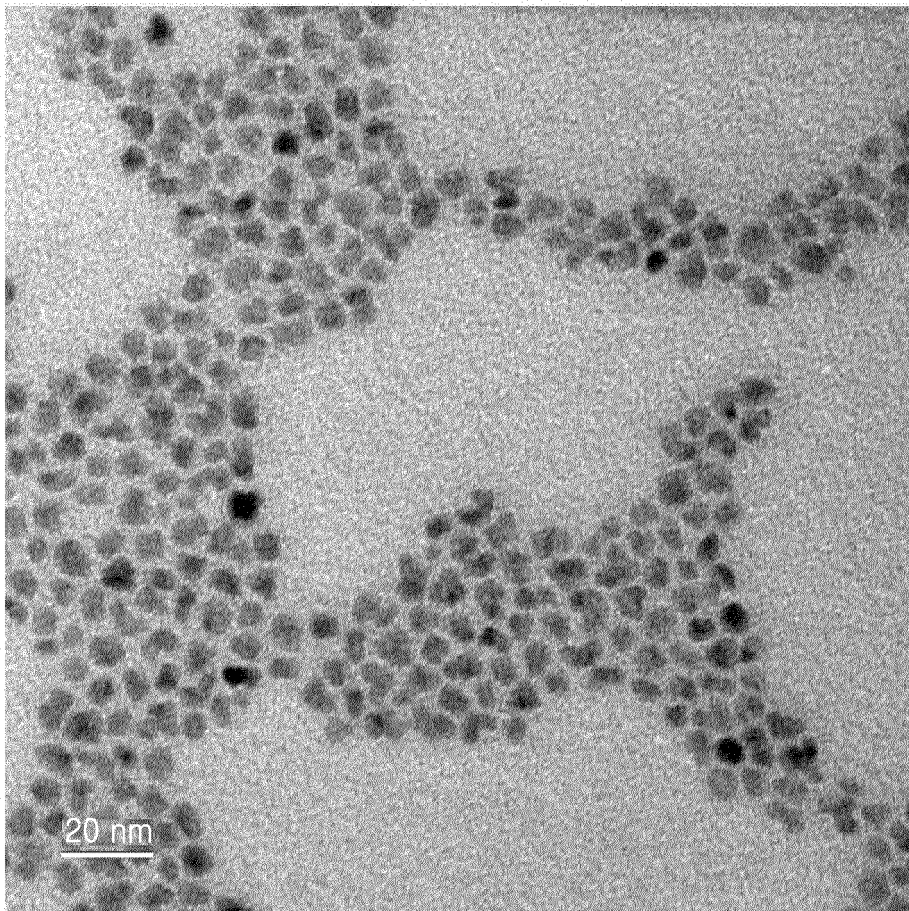


FIG. 11

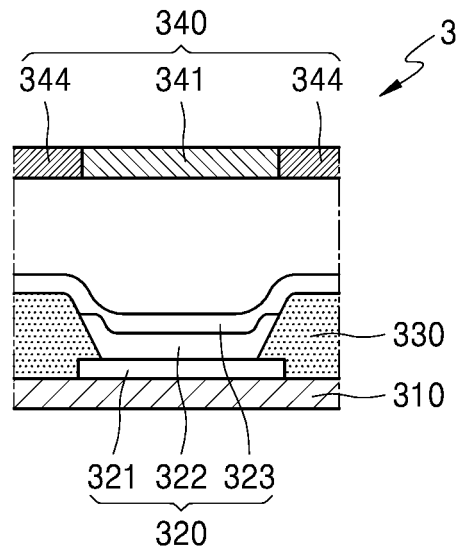
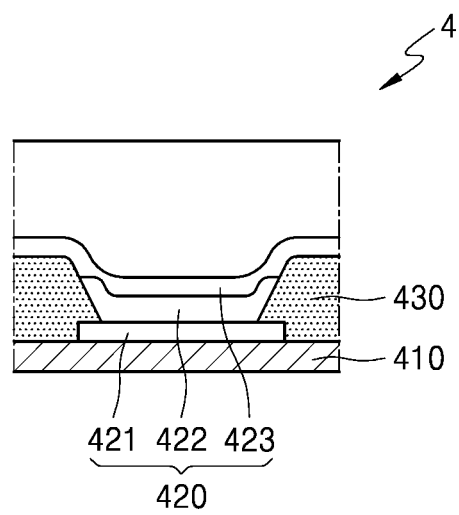


FIG. 12



INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2020/095124

A. CLASSIFICATION OF SUBJECT MATTER C09K 11/02(2006.01); C09K 11/88(2006.01); B82Y 20/00(2011.01)n According to International Patent Classification (IPC) or to both national classification and IPC																		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C09K 11/02(2006.01); B82B 1/00(2006.01); B82B 3/00(2006.01); B82Y 20/00(2011.01); B82Y 40/00(2011.01); C01G 11/00(2006.01); C01G 13/02(2006.01); C09K 11/08(2006.01); C09K 11/88(2006.01) Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Korean utility models and applications for utility models: IPC as above Japanese utility models and applications for utility models: IPC as above Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) eKOMPASS (KIPO internal) & keywords: 반도체(semiconductor), 클러스터(cluster), ZnSe, ZnSeTe, ZnS, 코어(core), 셸(shell)																		
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>A</td> <td> KR 10-2011-0133405 A (KOREA INSTITUTE OF SCIENCE AND TECHNOLOGY) 12 December 2011 (2011-12-12) See claims 1 and 11; and paragraph [0020]. </td> <td>1-20</td> </tr> <tr> <td>A</td> <td> JP 2010-132906 A (LIFE TECHNOLOGIES CORP.) 17 June 2010 (2010-06-17) See entire document. </td> <td>1-20</td> </tr> <tr> <td>A</td> <td> KR 10-2017-0117619 A (NANOCO TECHNOLOGIES LTD.) 23 October 2017 (2017-10-23) See entire document. </td> <td>1-20</td> </tr> <tr> <td>A</td> <td> KR 10-2019-0113323 A (DAEGU GYEONGBUK INSTITUTE OF SCIENCE AND TECHNOLOGY) 08 October 2019 (2019-10-08) See entire document. </td> <td>1-20</td> </tr> <tr> <td>A</td> <td> KR 10-2016-0120632 A (KOREA INSTITUTE OF SCIENCE AND TECHNOLOGY) 18 October 2016 (2016-10-18) See entire document. </td> <td>1-20</td> </tr> </tbody> </table>	Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	A	KR 10-2011-0133405 A (KOREA INSTITUTE OF SCIENCE AND TECHNOLOGY) 12 December 2011 (2011-12-12) See claims 1 and 11; and paragraph [0020].	1-20	A	JP 2010-132906 A (LIFE TECHNOLOGIES CORP.) 17 June 2010 (2010-06-17) See entire document.	1-20	A	KR 10-2017-0117619 A (NANOCO TECHNOLOGIES LTD.) 23 October 2017 (2017-10-23) See entire document.	1-20	A	KR 10-2019-0113323 A (DAEGU GYEONGBUK INSTITUTE OF SCIENCE AND TECHNOLOGY) 08 October 2019 (2019-10-08) See entire document.	1-20	A	KR 10-2016-0120632 A (KOREA INSTITUTE OF SCIENCE AND TECHNOLOGY) 18 October 2016 (2016-10-18) See entire document.	1-20
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.																
A	KR 10-2011-0133405 A (KOREA INSTITUTE OF SCIENCE AND TECHNOLOGY) 12 December 2011 (2011-12-12) See claims 1 and 11; and paragraph [0020].	1-20																
A	JP 2010-132906 A (LIFE TECHNOLOGIES CORP.) 17 June 2010 (2010-06-17) See entire document.	1-20																
A	KR 10-2017-0117619 A (NANOCO TECHNOLOGIES LTD.) 23 October 2017 (2017-10-23) See entire document.	1-20																
A	KR 10-2019-0113323 A (DAEGU GYEONGBUK INSTITUTE OF SCIENCE AND TECHNOLOGY) 08 October 2019 (2019-10-08) See entire document.	1-20																
A	KR 10-2016-0120632 A (KOREA INSTITUTE OF SCIENCE AND TECHNOLOGY) 18 October 2016 (2016-10-18) See entire document.	1-20																
☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.																		
<table border="0"> <tr> <td style="vertical-align: top;"> * Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "D" document cited by the applicant in the international application "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed </td> <td style="vertical-align: top;"> "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family </td> </tr> </table>	* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "D" document cited by the applicant in the international application "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family																
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "D" document cited by the applicant in the international application "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family																	
<table border="1"> <tr> <td>Date of the actual completion of the international search 06 May 2021</td> <td>Date of mailing of the international search report 13 May 2021</td> </tr> </table>	Date of the actual completion of the international search 06 May 2021	Date of mailing of the international search report 13 May 2021																
Date of the actual completion of the international search 06 May 2021	Date of mailing of the international search report 13 May 2021																	
<table border="1"> <tr> <td> Name and mailing address of the ISA/KR Korean Intellectual Property Office Government Complex-Daejeon Building 4, 189 Cheongsaro, Seo-gu, Daejeon 35208 Facsimile No. +82-42-481-8578 </td> <td> Authorized officer Telephone No. </td> </tr> </table>	Name and mailing address of the ISA/KR Korean Intellectual Property Office Government Complex-Daejeon Building 4, 189 Cheongsaro, Seo-gu, Daejeon 35208 Facsimile No. +82-42-481-8578	Authorized officer Telephone No.																
Name and mailing address of the ISA/KR Korean Intellectual Property Office Government Complex-Daejeon Building 4, 189 Cheongsaro, Seo-gu, Daejeon 35208 Facsimile No. +82-42-481-8578	Authorized officer Telephone No.																	

Form PCT/ISA/210 (second sheet) (July 2019)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/KR2020/095124

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
KR 10-2011-0133405 A	12 December 2011	CN 102266740 A	07 December 2011
		CN 102266740 B	16 April 2014
		JP 2011-255494 A	22 December 2011
		JP 5514126 B2	04 June 2014
		KR 10-1195771 B1	05 November 2012
		US 2011-0297871 A1	08 December 2011
		US 8507094 B2	13 August 2013
JP 2010-132906 A	17 June 2010	AU 2002-367778 A1	10 November 2003
		CA 2453450 A1	06 November 2003
		EP 1409240 A2	21 April 2004
		EP 1409240 B1	09 May 2012
		EP 2218762 A2	18 August 2010
		EP 2218762 A3	29 September 2010
		JP 2005-519782 A	07 July 2005
		JP 4567436 B2	20 October 2010
		US 2003-0017264 A1	23 January 2003
		US 2006-0057382 A1	16 March 2006
		US 2007-0125983 A1	07 June 2007
		US 6815064 B2	09 November 2004
		US 7172791 B2	06 February 2007
		WO 03-092043 A2	06 November 2003
		WO 2003-092043 A3	29 January 2004
KR 10-2017-0117619 A	23 October 2017	CN 105705611 A	22 June 2016
		CN 105705611 B	29 June 2018
		CN 108751248 A	06 November 2018
		CN 108751248 B	26 February 2021
		EP 3044287 A1	20 July 2016
		EP 3044287 B1	12 September 2018
		JP 2016-539908 A	22 December 2016
		JP 2018-135266 A	30 August 2018
		JP 6313860 B2	18 April 2018
		JP 6570688 B2	04 September 2019
		KR 10-1788241 B1	19 October 2017
		KR 10-2016-0055237 A	17 May 2016
		TW 201514101 A	16 April 2015
		TW 201641428 A	01 December 2016
		TW 201827344 A	01 August 2018
		TW I557076 B	11 November 2016
		TW I655156 B	01 April 2019
		TW I661993 B	11 June 2019
KR 10-2019-0113323 A	08 October 2019	US 2015-0076494 A1	19 March 2015
		WO 2015-036762 A1	19 March 2015
		CN 111971367 A	20 November 2020
KR 10-2016-0120632 A	18 October 2016	EP 3760692 A1	06 January 2021
		WO 2019-190147 A1	03 October 2019
		CN 106058023 A	26 October 2016
		US 2016-0300981 A1	13 October 2016
		US 9842962 B2	12 December 2017

Form PCT/ISA/210 (patent family annex) (July 2019)